New Polyelectrolyte Materials for High Temperature Fuel Cells

John B. Kerr
Lawrence Berkeley National Laboratory (LBNL)
Collaborators:
Los Alamos National Laboratory (LANL).
3M Company

May17, 2007

Project ID #
FCP33

Overview

Timeline

- Project start – February 2007
- Project end – September 2010
- Percent complete – 5%

Budget

- Total project funding
  - DOE share $6,000k
  - Contractor share $1,000k in-kind
- Funding received in FY06 - $0
- Funding for FY07 - $1150k

Barriers

E. System Thermal and Water Management.

B. Stack Material and Manufacturing Cost.

A. Durability

C. Electrode Performance.

Team/Partners

- Nitash Balsara, Rachel Segalman, Adam Weber (LBNL).
- Bryan Pivovar, James Boncella (LANL)
- Steve Hamrock (3M Company)

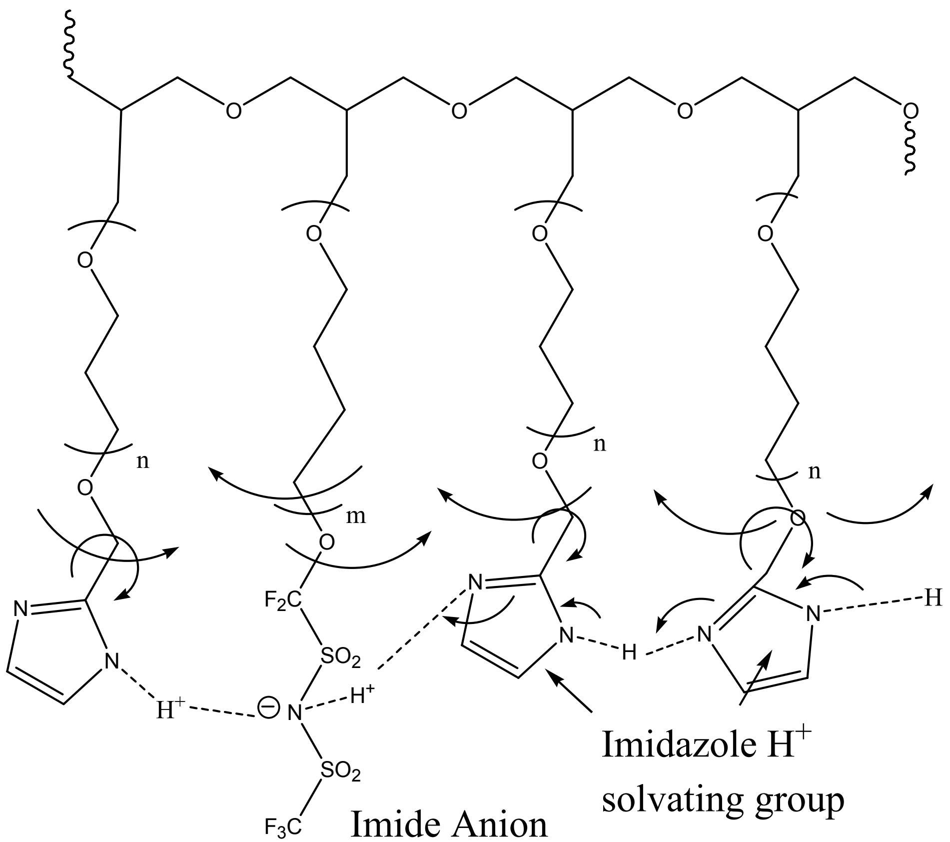
Objectives

- Investigate the use of solid polyelectrolyte proton conductors that do not require water.
- Prepare solid electrolytes where only the proton moves.
- Significant system simplifications for Fuel Cells.
  - Heat and water management greatly simplified.
  - Provide Car Manufacturers with Next Generation Materials that facilitate competitive Fuel Cell Vehicles.

Approach

- Measure conductivity, mechanical/thermal properties of Nafion®, 3M PFSA and other polyelectrolytes doped with imidazoles. Compare with water doped materials (FY07-08)
- Covalently attach imidazoles to side chains of ionomers with appropriate polymer backbones and test for conductivity, mechanical/thermal/chemical behavior and gas permeability (FY07-08).
- Prepare composite electrodes and operate MEAs without humidification (FY08-10).
- Develop Structure-Function relationships for polymer design. (FY09-10).

APPROACH
Tether Imidazoles and Acid Groups to Polymers



Side chains structures facilitate durability studies – small molecule fragments.

- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature and length of side chain to control mobility.
- Control mechanical & morphological properties by altering backbone and use of block co-polymers.
  - Polystyrene, Polynorbornene and Poly(arylene ether) backbones.
- **Promote Grotthuss Proton Transport → 10^{-1}S/cm**

Summary of Prior Work (LBNL)
(2003 –present)

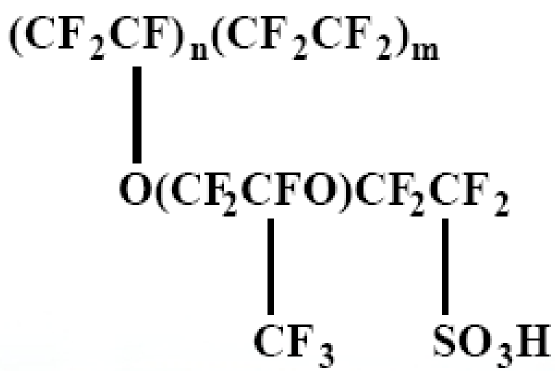
- Proton Conductivities of completely solid state polyelectrolytes with a tethered imidazole solvation group show little loss of conductivity compared to polyelectrolytes doped with free solvent imidazole.
- Phase separation and polymer morphology are critical for promotion of fast proton mobility (Grotthuss mechanism) and selectivity in gas transport.
- A road map exists on how to attain solvent-free membranes with attractive proton conductivities (close to 0.1 S/cm):
  - Nature and concentration of acid group, polymer morphology, C-tethered imidazole present in large excess for Grotthuss proton transport.
- Keep imidazole protonated in electrode to prevent platinum catalyst poisoning – use non-Pt catalysts.
- Imidazole doped PFSA appears to reject water.
  - Minimizes swelling and freezing issues.
  - **PFSA with tethered imidazole may be most durable membrane.**

Summary of Prior Work (LANL) (2003 –present)

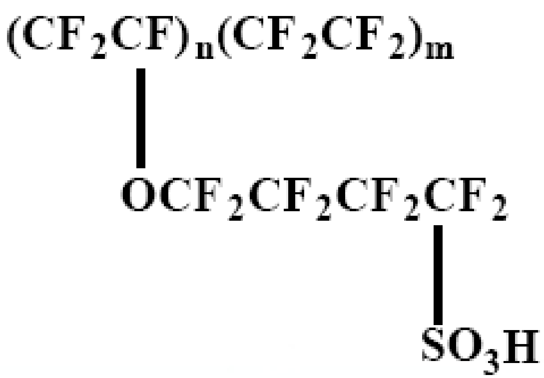
- Prepared and tested Polynorbornenes:
  - Attached imidazolium ions (not Grotthus capable).
  - Prepared block co-polymers.
  - Measured good conductivities (0.035S/cm at low RH(10%) when doped with phosphoric acid.
- Developed transport measurements for non-Nafion® membranes
- Developed composite electrode and MEA fabrication methods for non-Nafion® materials
  - Reduced High Frequency resistance
  - Non-Nafion® materials exhibit gas transport limitations.

Summary of Prior Work (3M Company)

- See Poster Presentation FCP32



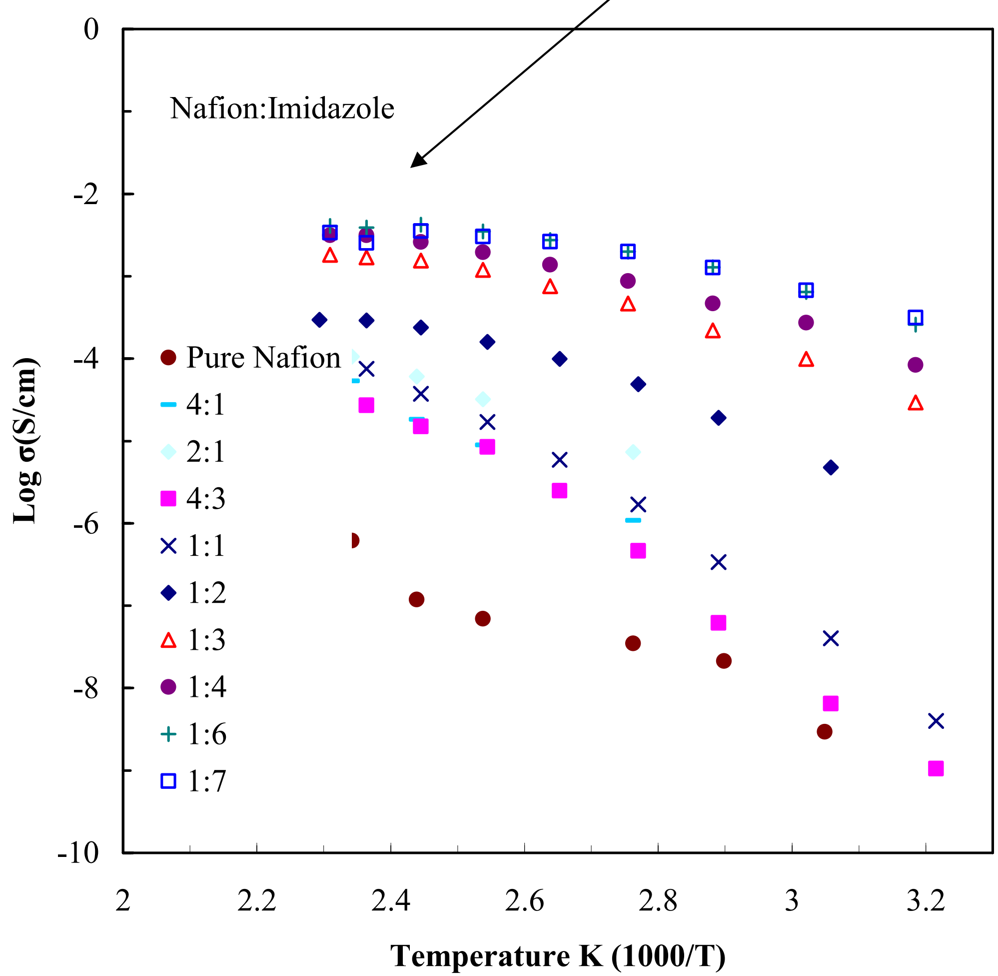
Standard Nafion® PFSA



New 3M PFSA

Conductivities of Imidazole Doped Nafion® Films

Flat temperature dependence consistent with Grotthuss Mechanism



Details of film casting

Nafion®: acid form

Equivalent MW: 1,100

Solvent used: aliphatic alcohol and water mixed solvent.

Drying condition: 65°C for 2 hours.

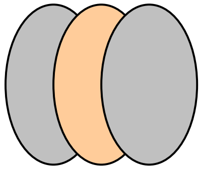
Film thickness: 100 μm ±20 μm

Testing conditions

Film between two parallel stainless steel plate.

Impedance measurements.

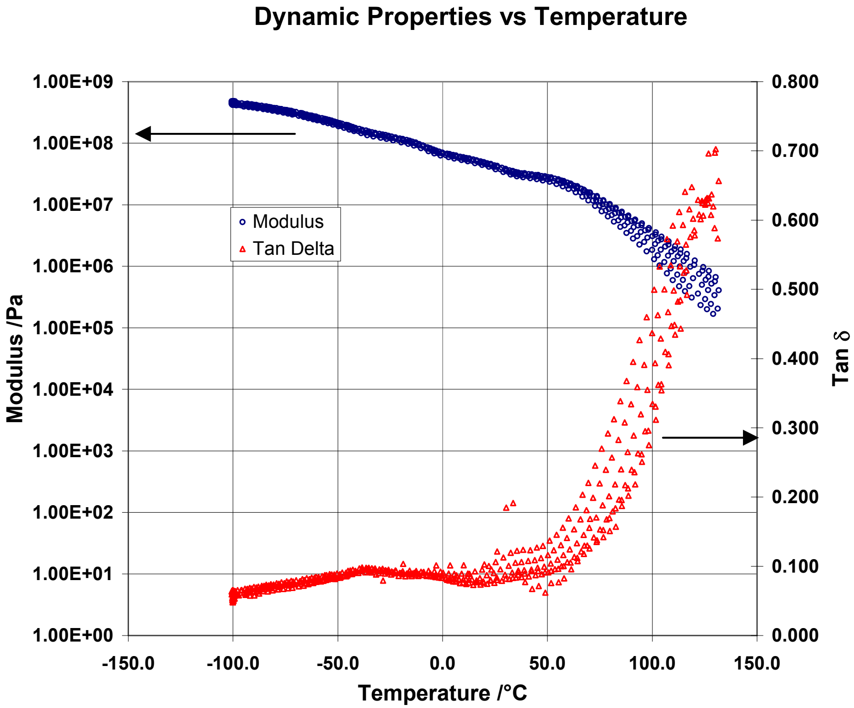
Decreasing temperature from 170°C to 25°C.



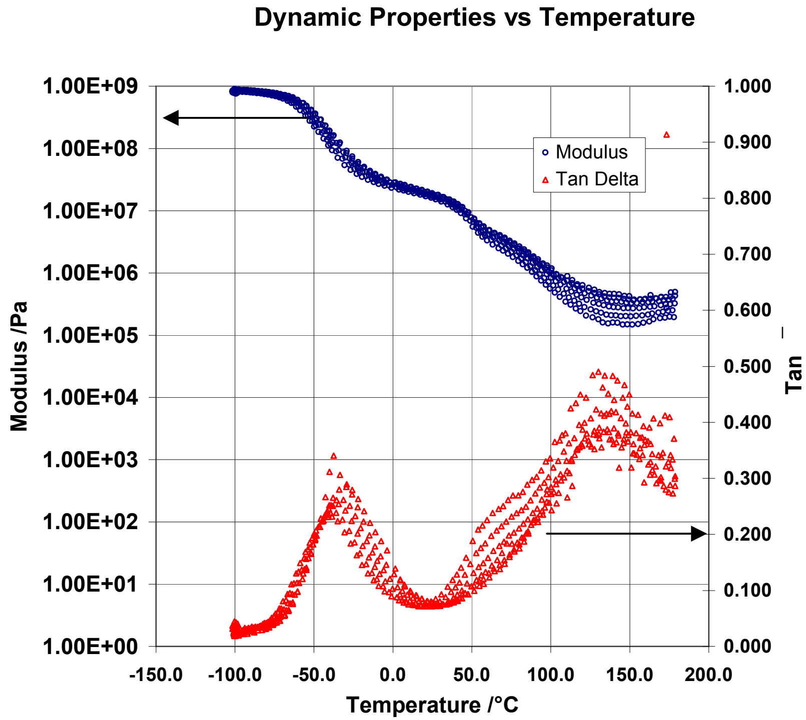
Stainless steel disc-Membrane-Stainless steel disc

DMA of Nafion® and Nafion®-Imidazole

Dry Cast Nafion®

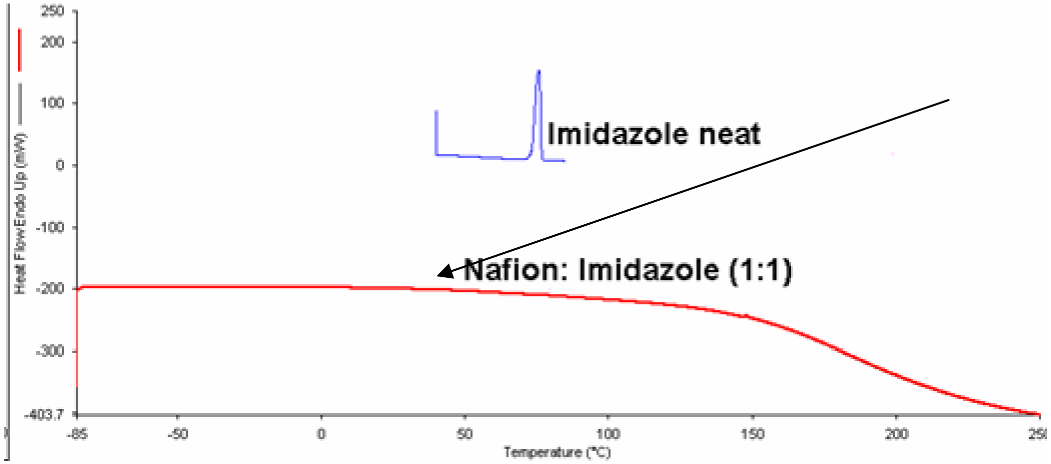


Dry Cast Nafion®-Imidazole SO_3H:Im 1:4

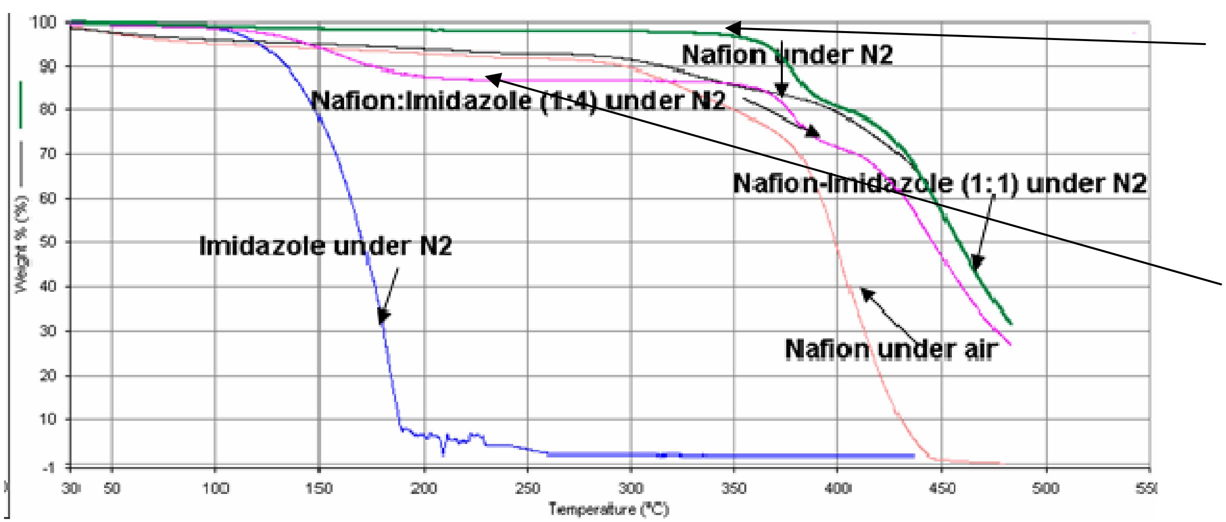


- Imidazole results in an increase in the T_g of Nafion® from 120°C to 140°C due to better dissociation of the protons and the formation of the imidazolium salt.
- Transition at -40°C indicates plasticization of perfluorinated matrix by imidazole, indicating mobile polymer backbones and less phase separation.

DSC/TGA Analysis of Imidazole-doped Nafion®



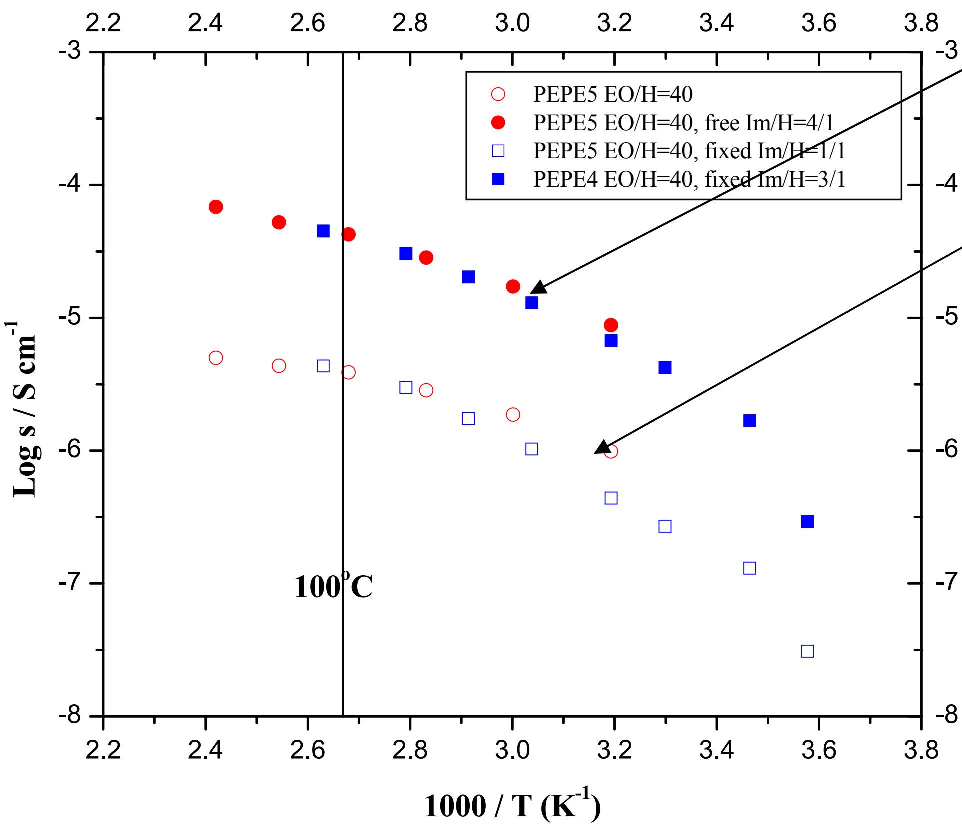
DSC shows no crystallization of Imidazole in Nafion® Matrix



- TGA shows no water uptake for Nafion®-Imidazole.
- Excess Imidazole Sublimes out
- Imidazole must be chemically bound.

Conductivities of free imidazole and fixed imidazole based proton conductors.

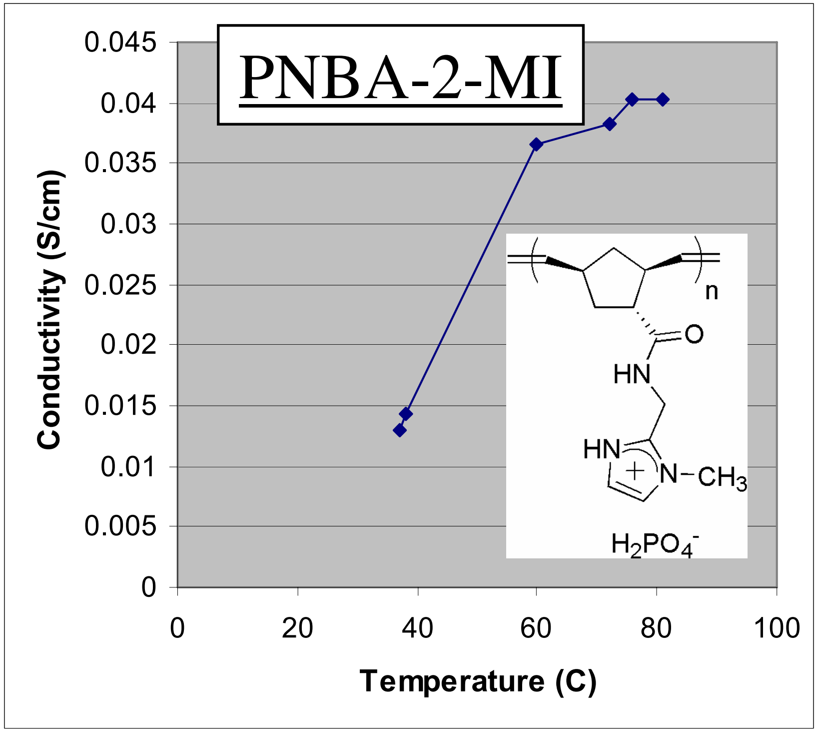
Alkylsulfonic acid groups fixed to polyepoxide polyethers.

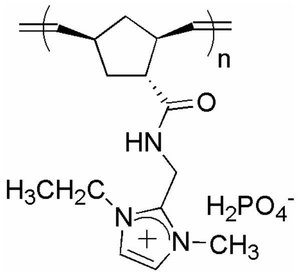


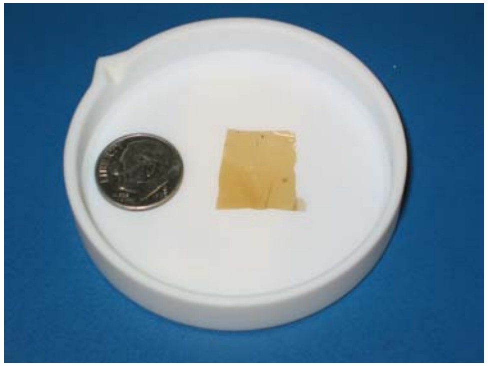
- **Conductivity of fixed Imidazole polymer equal to the conductivity of the polymer doped with free imidazole solvent.**
- Relative concentration of Imidazole to acid group is critical.
- Increase conductivity by optimiz-ation of tether length, acid/base concentration, nature of the acid group (Fluoroalkylsulfonylimides vs. Alkylsulfonate.
- Polymer matrix and imidazole unable to particpate in Grotthuss transport.

➔**Road Map to solvent-free conductivity above 10^{-2}S/cm exists.**

Membrane Conductivity Dependence on Water Content







PNBA-2E5MI

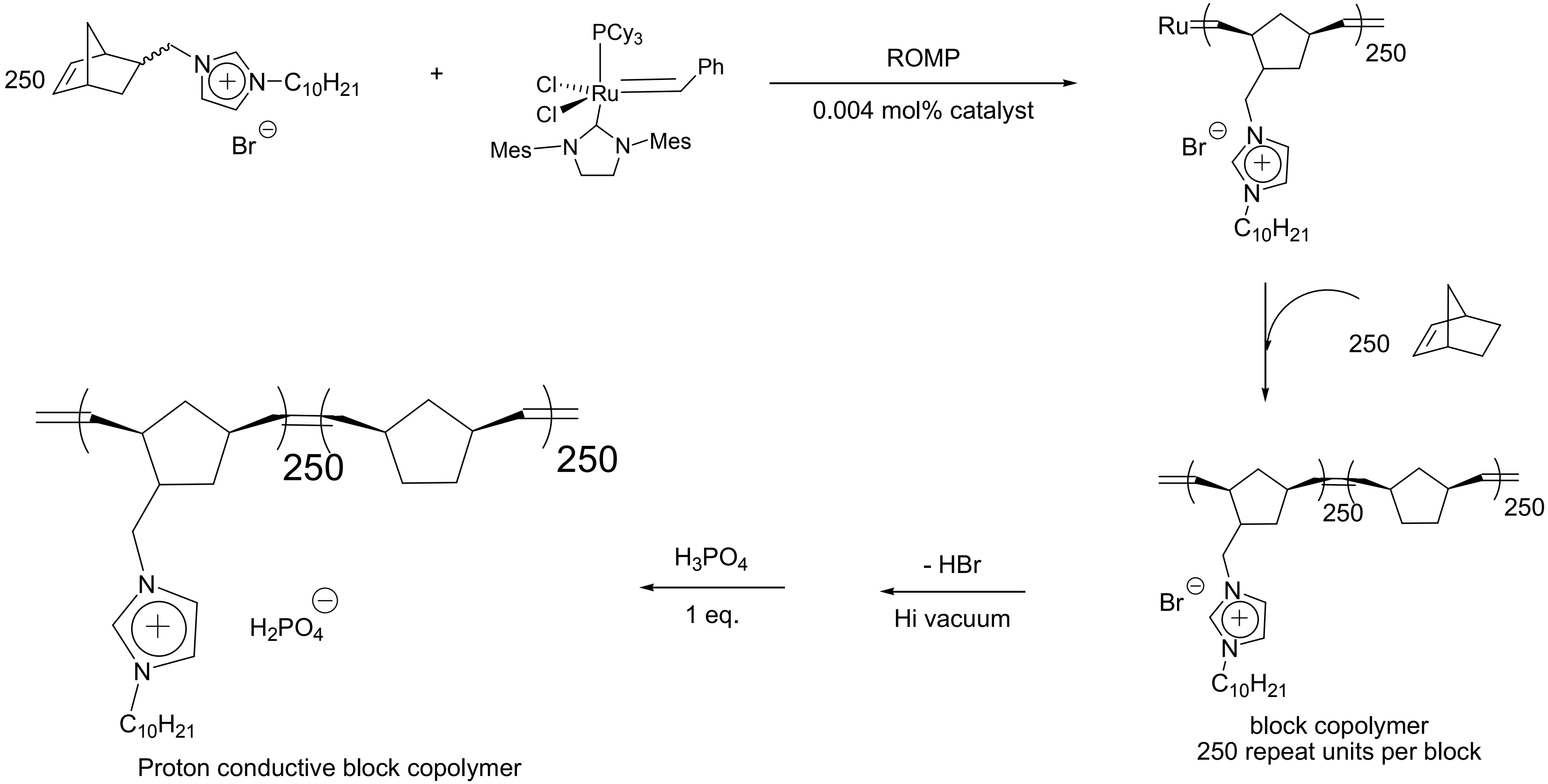
Conductivity (90˚C)	Relative Humidity
0.035 S/cm	10%
0.047 S/cm	25%

- PNBA-2-MI phosphate is water soluble, but shows reasonable conductivity even in the dry state
- The role of the phosphate anion and proton in conduction needs to be clarified

- PNBA-2E5MI is the ethylated version of PNBA-2-MI and is also water soluble, but likewise shows reasonable conductivity at low RH

Los Alamos
NATIONAL LABORATORY

NBE-Imidazole Copolymer



Los Alamos NATIONAL LABORATORY

Technical Approaches

Task 1 Interface

Membrane-Electrode Interface

- Interfacial resistance measurement
- Interfacial failure mechanism
- Membrane property criteria

Task 2 Membrane

Membrane Design

- Effect of hydrophobic fluorine
- Effect of specific interaction
- Electrochemical properties

Task 3 Electrode

Electrode Ionomer Design

- Water/alcohol based catalyst ink
- H_2/air fuel cell performance
- Electrochemical analysis

Task 4 Durability

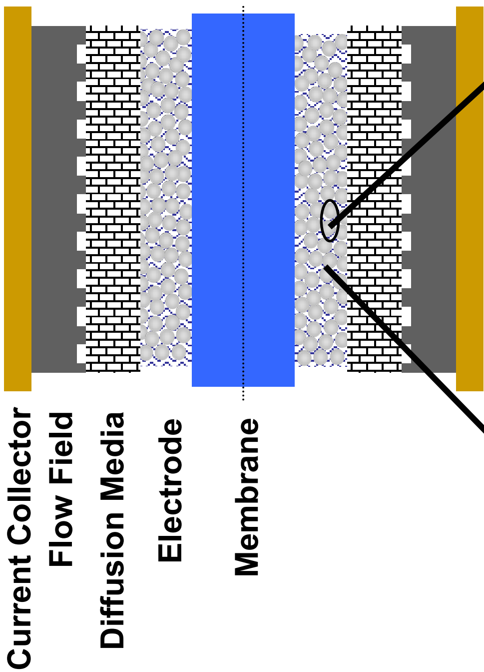
Long-Term Fuel Cell Test

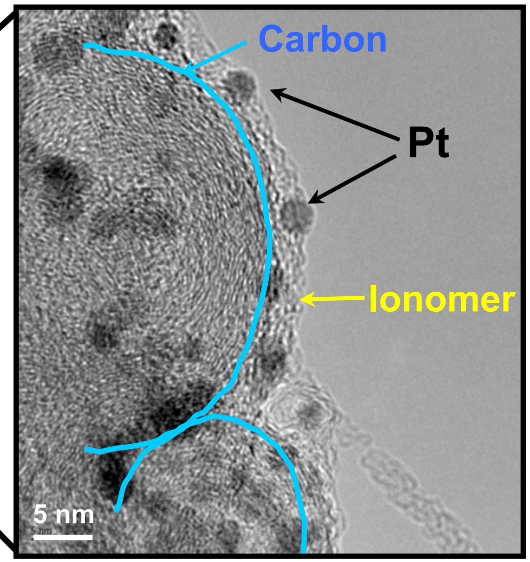
- Fully hydrated conditions
- Start-stop test
- High T, low RH H_2/air conditions

Los Alamos NATIONAL LABORATORY

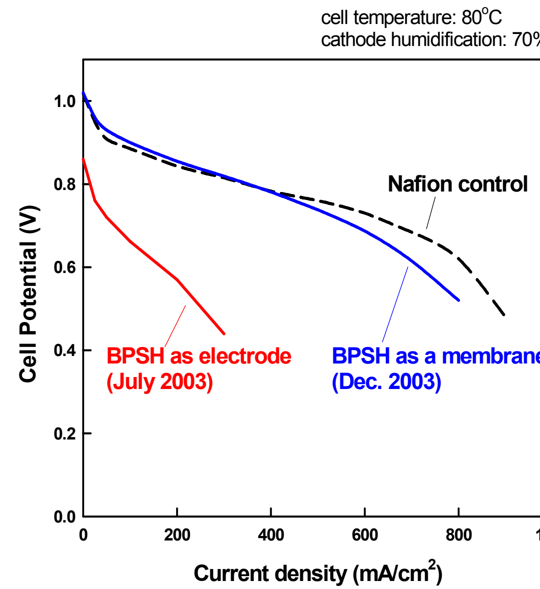
Electrode

Electrode Ionomer Design





HR-TEM images of
Nafion®-bonded catalyst layer*



Nafion® Ionomer Binder

High reactant permeability (H_2, methanol, O_2)
High proton conductivity
Chemically inert
Created porous structure
Optimized performance (only binder 15+ yrs)

Non-Nafion® Ionomer Binder

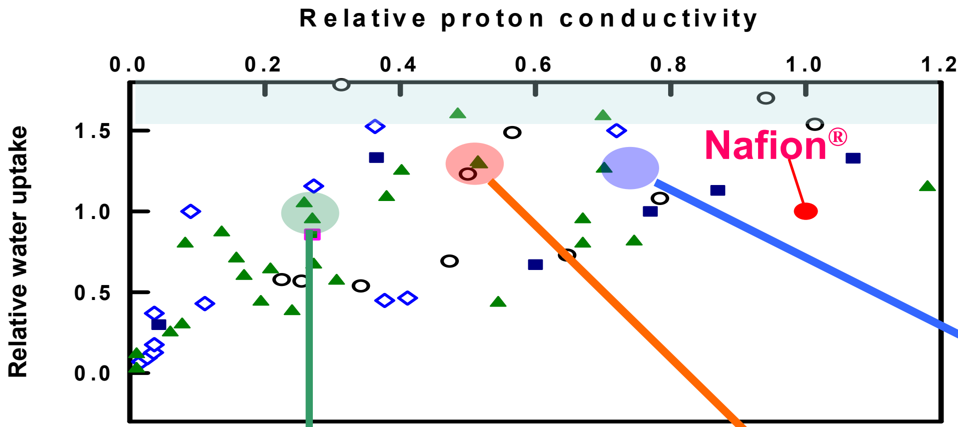
Good interfacial compatibility with non-Nafion® membranes
Good high temperature stability
Tailored chemical structure
LANL started research from 2003

Los Alamos NATIONAL LABORATORY

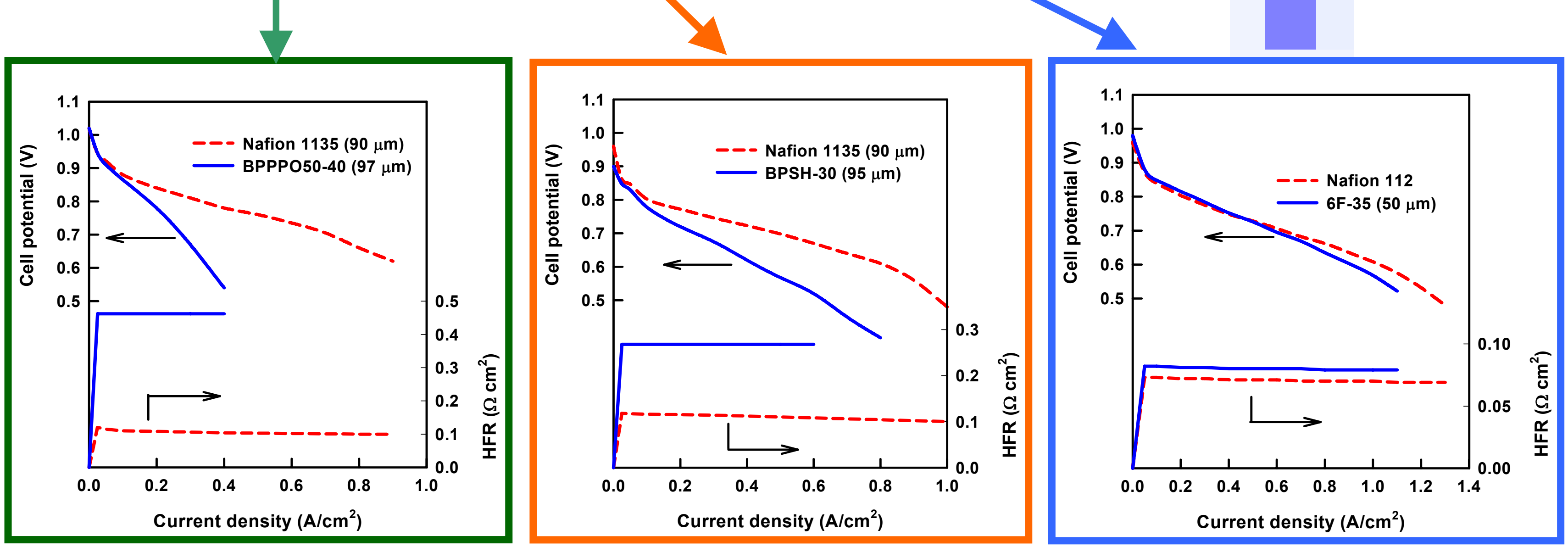
*Ref. Karren More, DOE Hydrogen and Fuel Cells Annual Report (2005)

Membrane

Fuel Cell Performance of Non-Nafion® Membranes



DOE FY'05 performance target (200 mW/cm² at 0.8 V) was accomplished

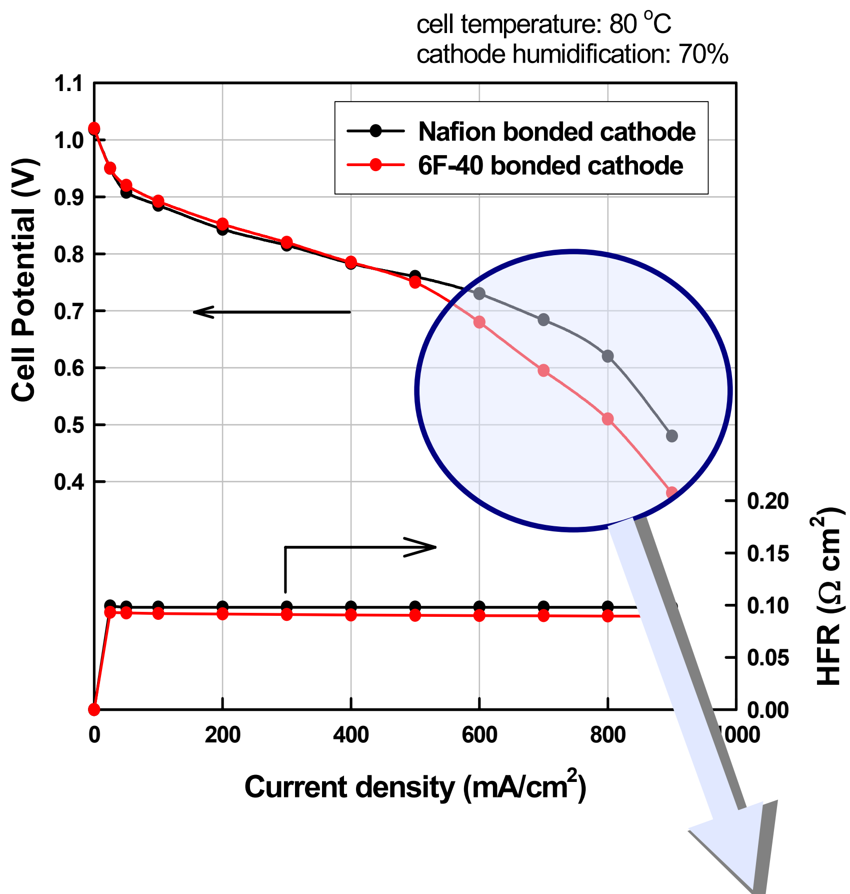


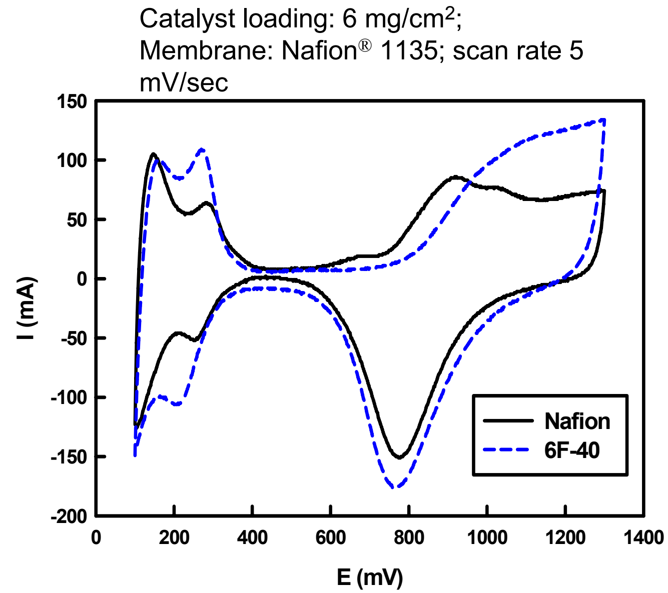
Catalyst: standard Pt/C (20%), 0.2 mg/cm²

Los Alamos
NATIONAL LABORATORY

Electrode

Fuel Cell Performance of Non-Nafion® Bonded Electrode from Alcohol Based Dispersion





- Electrochemical active surface area 6F-40 electrode ≃ Nafion® electrode,
- Hydrogen oxidation and reduction occur at very similar rates with a noticeable difference in the hydrogen desorption and oxidation peak shapes.

Non-Nafion® bonded cathode suffered from mass transfer limitation !!!

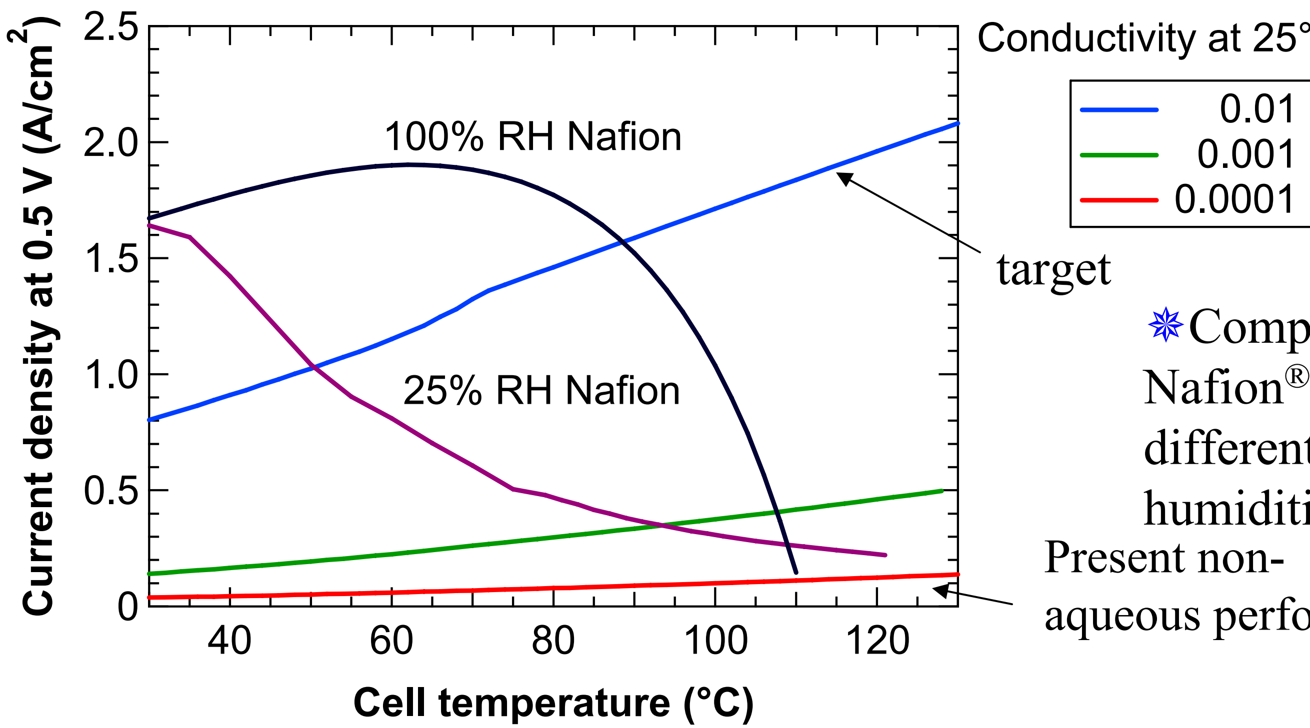
Los Alamos
NATIONAL LABORATORY

Future Work -Who does What & When?

- **LBNL-Kerr/Balsara/Segalman/Weber**
  - Random and Block copolymer synthesis (FY07-10) – Kerr/Balsara
  - Tether acid and imidazole groups to polymers.(FY07-08) - Kerr/Balsara
  - Mechanical, morphological and electrochemical characterization of materials.(FY07-10) - Kerr/Balsara/Segalman
  - Chemical and mechanical stability.(FY07-10) - Kerr
  - System modeling (FY07-10) - Weber
- **LANL - Pivovar/Boncella**
  - Block copolymer synthesis of polynorbornene and poly(arylene ether) polymers.(FY07-08)- Boncella
  - Transport measurements (conductivity, gas crossover)(FY07-08), cell testing and MEA preparation/testing(FY08-10). Pivovar
- **3M - Hamrock**
  - Provide PFSA material for testing and explore attachment of imidazole (FY07-08).
  - Durability and chemical stability(FY07-10).
  - MEA preparation and testing (FY09-10).
- **U of Central Florida - Fenton**
  - Test membrane materials under HTMWG program (FY08-10)

System Modeling to Develop Decision Criteria

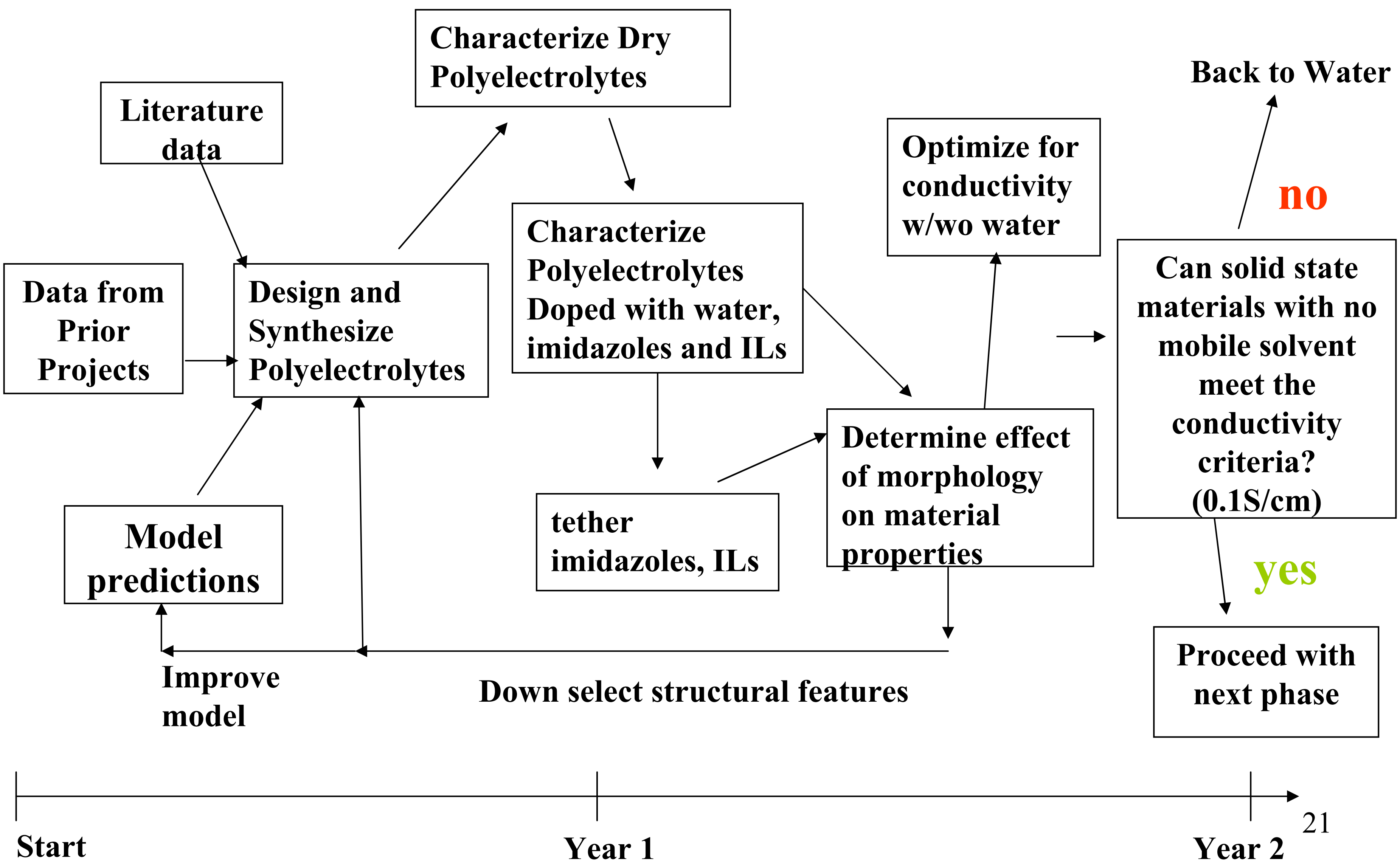
- Estimate suitability of membrane properties
  - Establish design targets and goals
- Analyze property and system tradeoffs
  - Examine distributions and limiting phenomena
- Ask and analyze "what if" questions
  - What conductivity do we really need?
  - **What if we have a membrane that rejects water?**



Present non-aqueous performance

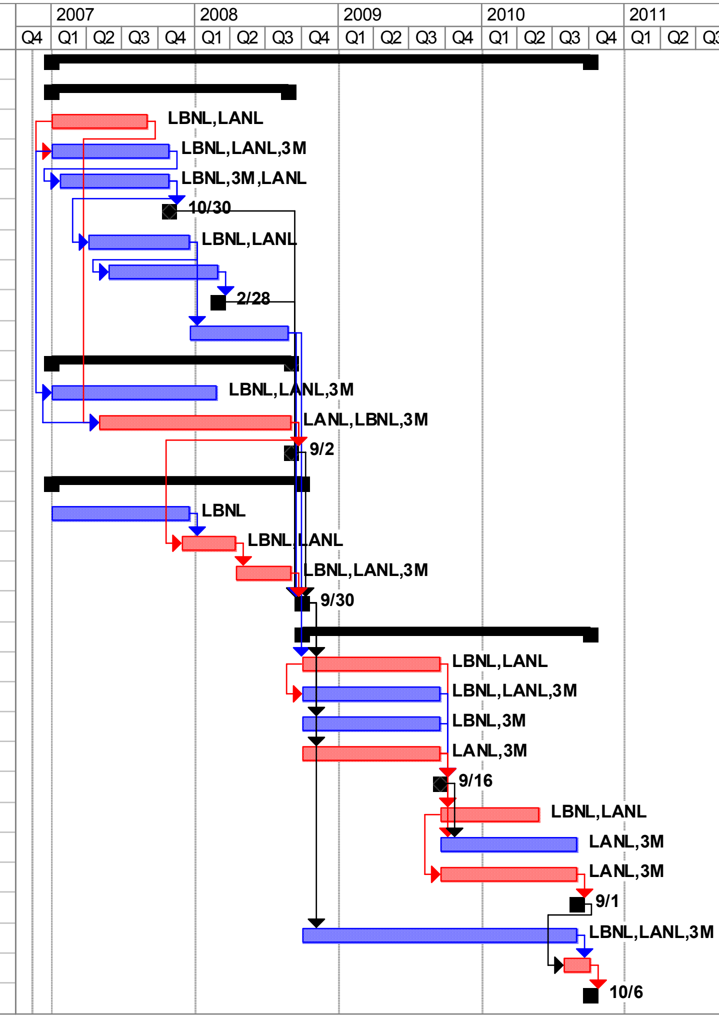
❈Compare performance to Nafion® 111 cell with different feed relative humidities

Work Flow- Years 1 & 2



Project Schedule

ID		Task Name
1		**New Polyelectrolyte Materials for Low Humidity Fuel Cells**
2		**Membrane Function**
3		Synthesis of Polyelectrolytes
4		Polymer characterization
5		Polymer characterization plasticized with imidazole, imidazolium IL and water
6		***Potential upper limit of conductivity estimated***
7		Attach imidazole and imidazolium IL to best polyelectrolyte
8		Characterize tethered materials
9		***Water and solvent free membrane materials characterized***
10		Further synthesis to optimize properties
11		**MEA properties**
12		Polymer Characterization as composite material
13		MEA Fabrication & Testing
14		***Initial correlation of polymer properties with MEA needs***
15		**Modeling**
16		Set up performance model
17		Validate model with data from MEA testing
18		Use model to predict necessary changes in performance targets.
19		***Go /No-Go Decision on replacement of water***
20		**Optimization of Materials for MEA Operation and Durability**
21		Synthesis of modified materials to optimize properties for MEA and membrane
22		Characterization of modified materials
23		Accelerated Durability testing and post-mortem analysis
24		Fabrication and testing of MEAs
25		***Correlation of Accelerated durability, post-mortem analysis and MEA tests***
26		Synthesis of materials to test for durability properties
27		Optimization of MEA structures
28		Acclerated durability testing in MEAs
29		***Decision on need for Perfluorinated materials***
30		Continued performance modeling with data from testing
31		Final Report recommendation for material design to achieve DOE goals.
32		***recommendation for material design to achieve DOE goals.***



Summary

- **Are membranes possible with conductivities of 0.1 S/cm without water?**
- **Attach heterocyclic bases (imidazole) to polyelectrolyte frameworks**
  - **Vary acid (fluoroalkylsulfonate, fluoroalkylsufonylimide)**
  - **Vary Imidazole and acid concentrations**
  - **Vary morphology and phase separation by change of backbone and block copolymer structures.**
  - **Is Grotthuss proton transport possible without water?**

Summary- questions to be answered.

- Is 0.1 S/cm conductivity necessary?
  - System simplifications allow lower conductivities?
- How does morphology affect gas crossover?
- What is the chemical and mechanical durability?
- What polymers lead to water rejection?
- Are PFSA polymers the most durable and do they reject water?